Complex synthesis and characterisation.

Synthesis of *trans*-[$PtCl_2\{P(OC_6H_3$-2,4-$^tBu_2)_3\}_2$], 4a. A solution of [$PtCl_2(NCPh)_2$] (0.285 g, 0.642 mmol) and tris(2,4-di-*tert*-butylphenyl)phosphite (0.840 g, 1.289 mmol) in dichloromethane (10 ml) was stirred for 17h, after which time a colorless precipitate had formed. The precipitate was collected by filtration and then dried *in vacuo*, giving complex **4a**. Yield: 0.71 g, 71%. Anal. Calcd for $C_{84}H_{126}Cl_2O_6P_2Pt$: C, 64.7; H, 8.15. Found: C, 64.7; H, 8.3. ν_{max}/cm^{-1} (Pt-Cl): 373 (CsI disk). ^1H NMR (CD_2Cl_2): δ 1.27 [s, 54H, ^{t}Bu], 1.41 [s, 54H, ^{t}Bu], 6.94 [dd, 6H, J = 8.6 Hz, J = 2.4 Hz, aryl], 7.63 [d, 6H, J = 2.4 Hz, aryl] and 7.64 [d, 6H, J = 8.6 Hz, aryl]. ^{31}P-{^1H} NMR (CD_2Cl_2): δ 77.2 [s with Pt sat., J = 4392 Hz].

Synthesis of [$\{Pt(\mu$-Cl)$\{\kappa^2$-*P,C*-$P(OC_6H_2$-2,4-$^tBu_2)(OC_6H_3$-2,6-$^tBu_2)_2\}\}_2$], 5a.

A mixture of $K_2[PtCl_4]$ (0.100 g, 0.24 mmol) and tris(2,4-di-*tert*-butylphenyl)phosphite (0.155 g, 0.24 mmol) in 2-methoxyethanol (8 ml) was heated at reflux temperature for 14 hrs. The solvent was removed *in vacuo*, then dichloromethane (20 ml) was added. The mixture was filtered through a pad of celite that was then washed with dichloromethane (10 ml). The combined dichloromethane extracts were concentrated *in vacuo* and ethanol was added to induce precipitation. The supernatant was removed and the colorless precipitate was recrystallized from dichloromethane/ethanol to give the title complex. Yield: 0.175 g, 83 %. Anal. Cald for $C_{42}H_{62}ClO_3PPt$: C, 57.56; H, 7.13. Found: C, 57.32; H, 7.26. *Major isomer.* ^1H NMR ($CDCl_3$): δ 1.25 [s, 36H, ^{t}Bu, non-orthometalated ring], 1.26 [s, 18H, ^{t}Bu, orthometalated ring], 1.37 [s, 18H, ^{t}Bu, orthometalated ring], 1.44 [s, 36H, ^{t}Bu, non-orthometalated ring], 6.98 [dd, 4H, J = 8.5 Hz, J = 2.5 Hz, aryl, non-orthometalated ring], 7.05 [m, br, 2H, aryl, orthometalated ring], 7.34 [2H, partially obscured, aryl,

orthometalated ring], 7.37 [dd, br, 4H, J = 2.5 Hz, J ~ 1 Hz, aryl, non-orthometalated ring], 7.54 [dd, br, 4H, J = 8.5 Hz, J = 1.5 Hz, aryl, non-orthometalated ring]. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 81.2 [s with Pt sat., J = 7750 Hz]. *Minor isomer.* ^{1}H NMR ($CDCl_3$): δ 1.16 [s, 18H, ^{t}Bu, orthometalated ring], 1.21 [s, 36H, ^{t}Bu, non-orthometalated ring], 1.28 [s, 36H, ^{t}Bu, non-orthometalated ring], 1.37 [s, 18H, ^{t}Bu, non-orthometalated ring], 7.04 [dd, 4H, J = 8.5 Hz, J = 2.5 Hz, aryl, non-orthometalated ring], 7.09 [m, br, 2H, aryl, orthometalated ring], 7.34 [m, br, 4H, partially obscured, aryl, non-orthometalated ring], 7.43 [dd, 4H, J = 8.5 Hz, J = 1.5 Hz, aryl, non-orthometalated ring], 7.51 [m, br, 2H, aryl, orthometalated ring]. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 79.8 [s with Pt sat., J = 7875 Hz].

Synthesis of [{Pt(μ-Cl){ κ^2-*P,C*-P(OC$_6$H$_2$-2,4-^{t}Bu$_2$)Ph$_2$}}$_2$], 5c. A mixture of $K_2[PtCl_4]$ (0.500 g, 1.205 mmol) and $P(OC_6H_3$-2,4-^{t}Bu$_2)Ph_2$ (0.471 g, 1.205 mmol) in *o*-xylene (30 ml) was heated at reflux temperature for 17 hours. The solvent was removed *in vacuo* and the product crystallized and then recrystallized from dichloromethane/methanol to give complex **5c** as a colorless solid. Yield: 0.224 g, 30%. Calcd for $C_{26}H_{30}ClOPPt$: C, 50.37; H, 4.88. Found: C, 50.24; H, 4.82. ^{1}H NMR of both isomers (ratio about 0.9:1, therefore absolute assignment not performed) ($CDCl_3$): δ 1.26 [s, 9H, ^{t}Bu], 1.32 [s, 9H, ^{t}Bu], 1.345 [s, 9H, ^{t}Bu], 1.350 [s, 9H ^{t}Bu], 7.03 [dd, br, 1H, J ~ 2 Hz, J ~ 2 Hz, aryl, orthometalated ring of one isomer], 7.04 [dd, br, 1H, J ~ 1.5 Hz, J ~ 3 Hz, aryl, orthometalated ring of second isomer], 7.36 – 7.53 [complex multiplets, 14H, *m*- and *p*-H's of Ph (both isomers) and 1 x aryl of orthometalated rings for both isomers], 7.83 [m, 4H, *o*-H of Ph (one isomer)], 7.93 [m, 4H, *o*-H of Ph (second isomer)]. ^{31}P-{^{1}H} NMR: δ 114.6 [s with Pt sat., J = 5216 Hz, one isomer], 114.2 [s with Pt sat., J = 5243 Hz, second isomer].

Synthesis of [{Pt(μ-Cl){ κ^2-*P,C*-P(OC_6H_2-2,4-$^tBu_2$)$^iPr_2$}}$_2$], 5d.

This complex was prepared by an analogous method used for the synthesis of **5c** using P(OC_6H_3-2,4-$^tBu_2$)$^iPr_2$ (0.389 g, 1.205 mmol) to give complex **5d** as a colorless solid. Yield: 0.028 g, 4%. Anal. Calcd for $C_{20}H_{34}ClOPPt$: C, 43.52; H, 6.21. Found: C, 43.04; H, 6.25. ^{1}H NMR of both isomer (ratio ~ 0.75:1) ($CDCl_3$): δ 1.23 – 1.43 [complex multiplets, CH_3 both isomers], 1.26 [s, 9H, ^{t}Bu, major isomer], 1.29 [s, 9H, ^{t}Bu, minor isomer], 1.32 [s, br, 1 x ^{t}Bu of each isomer], 2.39 [q, 1H, J = 7 Hz, PC*H*, minor isomer], 2.47 [q, 1H, J = 7 Hz, PC*H*, major isomer], 6.94 [m, 1 x aryl of each isomer], 7.38 [dd, 1H, J ~ 2 Hz, J ~ 2 Hz, aryl, major isomer], 7.53 [dd, 1H, J ~ 2 Hz, J ~ 2 Hz, aryl, minor isomer]. ^{31}P-{^{1}H} NMR: δ 156.1 [s with Pt sat., J = 4993 Hz, major isomer], 155.4 [s with Pt sat., J = 4990 Hz, minor isomer].

Catalysis with 1.0 – 0.1 mol%[Pt]. Aryl halide (10 mmol), phenylboronic acid (1.829 g, 15 mmol), base (20 mmol) and the appropriate amount of catalyst were placed in a 3-necked flask equipped with reflux condenser with attached nitrogen inlet. The system was flushed with nitrogen and then solvent (30 ml) added. The mixture was then heated at the appropriate temperature for 18 hours, then cooled in an ice bath and HCl(aq) (2M, 100ml) added. The mixture was then extracted with dichloromethane (100 ml then 2 x 50 ml), the combined organic extracts washed with water (50 ml) and then dried (Mg_2SO_4). The solvent was removed under reduced pressure, then hexadecane (3 ml, 0.068M in toluene, internal standard) and dichloromethane were added and the conversion to product was then determined by GC analysis.

Catalysis with <0.1 mol%[Pt]. As above except that a 1ml solution of catalyst in dioxane at the correct concentration, made by appropriate dilution, was added with the solvent to the reaction mixture.

Table 1. Brief optimisation of solvents and bases.[a]

Solvent	Base	Temp. (°C)	Conv. (%)[b]
Toluene	K_2CO_3	110	49
1,4-dioxane	K_2CO_3	100	79
DMA	K_2CO_3	110	54
NMP	K_2CO_3	110	28
1,4-dioxane	K_3PO_4	100	100
1,4-dioxane	KF	100	90
1,4-dioxane	Cs_2CO_3	100	90
1,4-dioxane	NaOAc	100	4
1,4-dioxane	Et_3N	100	7
1,4-dioxane	KF/K_3PO_4 (1:1)	100	89

[a]Reaction conditions: 10 mmol 4-bromoacetophenone, 15 mmol $PhB(OH)_2$, 20 mmol base, 30 ml solvent, catalyst **5a** (0.1mol%), 18 h. [b]Conversion to product determined by GC, based on aryl bromide, hexadecane internal standard.

Figure 1. Plot of conversion against time in the coupling of 4-bromoacetophenone and phenylboronic acid catalysed by complex **5a** (0.001 mol%) – conditions as for table 1 in the main text.